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TITLE: Direct-Write Process for UV-Curable Epoxy Materials by Inkjet Technology

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TITLE: Materials Research Society Symposium Proceedings, Volume 758
Held in Boston, Massachusetts on December 3-5, 2002. Rapid Prototyping Technologies

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Direct-Write Process for UV-Curable Epoxy Materials by Inkjet Technology

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ABSTRACT

We demonstrate drop-on-demand inkjet printing technique to be a high throughput method for the patterned deposition of UV-curable epoxy materials. Different multi-nozzle printheads have been used to produce epoxy droplets with controlled volume in the range from 15 to 180 pl, and to apply the droplets with high placement accuracy. For a large dot grid pattern, which was printed by addressing 126 individual ink channels, standard deviations of $\sigma_x = 2.3 \mu\text{m}$ and $\sigma_y = 2.6 \mu\text{m}$ have been achieved for the error in dot placement. The deposited epoxy dots were found to form planar convex lenses with a focal length of 142 μm . In addition, we have successfully printed magnetic nanoparticles in a carrier fluid with the drop-on-demand printheads, as a step towards the production of composites.

INTRODUCTION

The ability of inkjet techniques to deposit a large variety of different materials, including polymers, material-precursors or dispersions of nanoparticles in fluidic media, makes it a highly flexible process for direct-write applications. The inkjet process is an additive non-contact method, and can be applied even on surfaces with pronounced topography. In particular multi-nozzle drop-on-demand inkjet printheads enable the deposition of patterned layers at a rate of several tens of cm^2 per second.

The versatility of this technique has been demonstrated for the production of different structures and devices in ceramic, electronic and MEMS applications [1-3]. Epoxy materials have been deposited before for applications in MEMS packaging and optics, but by using inkjet devices that are based on a single channel actuation [4]. We have recently reported the dispensing of epoxy materials for bonding applications using a multi-nozzle piezoelectric inkjet printhead [5].

In this paper we describe the dot diameters achievable for epoxy materials with the present day inkjet printing capabilities, their placement accuracy and their surface profiles. In addition, we present attempts to print geometric patterns with magnetic inks, indicating the potential of drop-on-demand inkjet printing for future applications in micro-manufacturing, specifically the printing of nanosized solid particles of ceramic, electrically conductive or magnetic materials for the production of complex hybrid devices.

EXPERIMENTAL DETAILS OF THE INKJET DEPOSITION METHOD

Piezoelectric drop-on-demand inkjet printheads from Xaar have been used in the experimental work presented herein to deposit epoxy materials onto different substrates. The mode of operation of these printheads is based on the generation of an acoustic wave within a small actuator channel due to an appropriate movement of the channel walls. This acoustic wave

creates the ejection of a single ink droplet through a well-defined nozzle at the end of the actuator channel [6, 7]. Xaar's different models of inkjet printheads comprise 126, 128 or 500 ink-channels in a linear arrangement. For most of the experiments described in this work an XJ126 printhead model with 126 channels was used (shown in Fig. 1). This printhead type delivers drop volumes of 50 pl or 80 pl for standard printheads, or variable drop volumes between 15 pl and 60 pl for a greyscale model. The drop repetition frequency for each channel is up to 7.5 kHz. Prototype printhead models with drop volumes down to 3-5 pl and as large as 180 pl are under development. The physical channel pitch of 137 μm results in a printing resolution of 185 dpi (dots per inch) with the printhead oriented at 90 degrees against the scanning direction, whereas higher resolutions, like 360 dpi, can be achieved by inclining the printhead appropriately, or by multiple printing while displacing the printhead for a fraction of its channel pitch.

Since the mechanism of drop formation is non-thermal, the stresses on both the printheads and the fluids are largely reduced in comparison with thermal inkjet techniques. Thus, a large variety of fluids and thermally sensitive liquids can be used, and high lifetimes of the printhead are guaranteed. Additionally, the XJ126 type printheads offer the possibility to adjust driving voltage levels and waveforms, to enable the drop ejection with different types of fluidic media. For the printheads used in this work, an additional passivation layer on the channel and electrode surface has been introduced, to avoid corrosion of these surfaces when aggressive fluids are used.

The XJ126 inkjet printhead is integrated into a custom-built computer-controlled flatbed printing set-up to be used for the deposition experiments. An xy-axis system based on linear motor drives is mounted on top of a heavy, vibration-damped granite table to ensure high printing accuracy and reliability. The x-axis, which holds the printhead on a height-adjustable fixture, is equipped with an LW7 linear motor stage from Anorad Corporation. During printing, this x-axis drive scans the printhead at a constant linear speed above the substrate surface, while a printhead controller addresses the appropriate channels of the printhead. The substrate is placed onto a vacuum table on the y-axis stage, which is driven by an Anorad LW10 drive. The usage of linear xy-drives allows for a high maximum velocity of 1.2 m/s, with an encoder resolution of 1 μm for the x-axis and 0.5 μm for the y-axis. The sample table can hold substrates up to 0.6×0.84 m in size. A Peltier element is integrated in the head mount fixture to be able to heat both the printhead and the ink supply, to extend the operation range of the printhead for liquids with higher viscosity. A slight vacuum is applied to the ink supply container, as the inkjet printhead needs a negative ink pressure in its channels during operation.

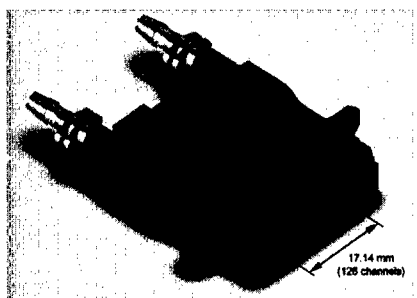


Figure 1. The XJ126 printhead model with 126 channels in a linear arrangement.

SELECTION AND CHARACTERIZATION OF EPOXY MATERIALS

A variety of single component, UV-curable epoxy materials with different viscosities and surface tensions have been characterized and tested for the deposition experiments with the Xaar inkjet printhead. The chosen materials were suited for optical and bonding applications.

Table I summarizes the relevant rheological parameters and the curing mechanism of the tested epoxy materials. The viscosity values were measured with a *StressTech* Rheometer from Reologica Instruments, and the static surface tension was obtained using the Du-Nouy ring method. Epoxy X1, X3 and X4 were only curable by UV-light, and required a radiation of 100 mW/cm^2 for 1-2 minutes at a wavelength of 300-400 nm for the curing process. Epoxy X2 was additionally curable at temperatures above 130°C .

An important parameter for the ability to eject droplets with a piezoelectric inkjet printhead is the low viscosity of the fluidic materials, since the printhead design with its narrow channels restricts the flow of highly viscous liquids significantly. A reduction of the viscosity of the epoxy materials could be achieved by elevating the temperature, as shown in table I. Furthermore, epoxy materials with different values for the static surface tension were selected. This parameter influences the ability of the epoxy to wet a given substrate, but it has to be in a defined range for the use in an inkjet printhead.

The epoxy materials from table I were studied regarding the drop formation in an XJ126 inkjet printhead. A custom-built microscopic setup with stroboscopic illumination was used for this investigation, which allowed the visualization of ink droplets in flight. With Epoxy X1 a regular drop formation at frequencies up to 5 kHz was possible at 25°C , but with strong tendency for the ink-jet to break into a number of smaller satellite drops. Epoxy X2 allowed a stable drop formation up to frequencies of 3 kHz at 25°C , and with increased reliability and higher maximum frequencies up to 5 kHz at a temperature of 40°C . With samples X3 and X4 drop ejection was only possible at lower frequencies and at temperatures exceeding 40°C and 60°C , respectively. No clogging of the actuator channels and nozzles was observed with any of the tested epoxies, even for longer idling periods up to several days. This indicates that pre-curing of the epoxy materials inside the printhead was absent. As a result of these investigations Epoxy X2 was chosen for the further deposition experiments.

Table I. UV-curable epoxy materials tested for printing with the inkjet printheads.

Sample	Viscosity [mPa·s] at 25°C	Viscosity [mPa·s] at 40°C	Surface tension [mN/m] at RT	Curing
Epoxy X1	15	10	41.9	UV
Epoxy X2	85	45	42.5	UV + heat ($>130^\circ\text{C}$)
Epoxy X3	120	60	28.0	UV
Epoxy X4	205	95	40.0	UV

RESULTS AND DISCUSSION OF INKJET DEPOSITION EXPERIMENTS

An example of an array of deposited and cured epoxy dots on a silicon substrate is shown in Fig. 2. An optical micrograph of patterns with higher complexity can be seen in Fig. 3. All structures and dot patterns have been directly printed onto the substrate in one printing sweep while individually addressing the 126 channels of the inkjet printhead. In the case of the pattern in Fig. 2 only every 3rd channel was firing at a time, resulting in a dot array spacing of $411 \mu\text{m}$.

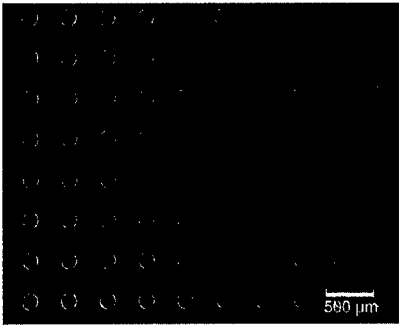


Figure 2. Array of cured epoxy dots with a spacing of 411 μm (printed with Epoxy X2 onto a silicon substrate).

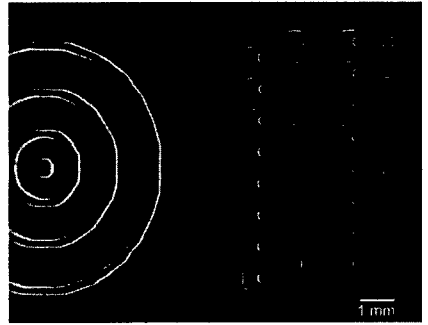


Figure 3. Examples of inkjet printed epoxy pattern (silicon substrate).

In order to evaluate the dot placement accuracy and repeatability when addressing 126 individual printhead channels, a dot array of more than 1×10^4 dots was printed onto a silicon substrate, cured and analysed optically using a Mitutoyo *Quick Vision* system. The pattern was deposited at a linear printing speed of 0.1 m/s, which corresponds to a drop repetition frequency of 730 Hz. The printhead-to-surface distance was kept constant at 1mm during printing.

A normal distributed error in dot placement was found (shown graphically in Fig. 4 for the x-direction). The placement error had standard deviations of $\sigma_x = 2.3 \mu\text{m}$ and $\sigma_y = 2.6 \mu\text{m}$ along the x- and y-direction, respectively. The mean dot diameter was 146 μm with $\sigma = 1.8 \mu\text{m}$, and the average error in circularity of the dots was found to be less than 1 μm . These results were achieved using an XJ126-300 printhead model, which delivers drop volumes of about 50 pl.

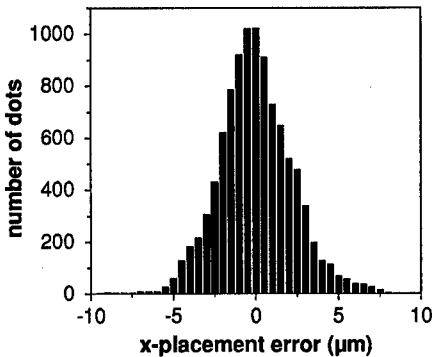


Figure 4. Dot placement error in x-direction (printing direction) for a pattern with 10^4 dots, $\sigma_x = 2.3 \mu\text{m}$.

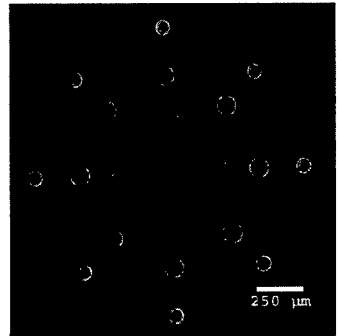


Figure 5. Dot pattern utilizing variable droplet volumes from a greyscale printhead, deposited in one printhead sweep (Epoxy X2 onto silicon).

A specific goal of this work was to produce different structure dimensions by varying the deposited droplet volumes. For this purpose a greyscale printhead was used, which is able to produce droplets in 4 different volume levels of 15, 30, 45 or 60 pl from each of its printhead channels. Fig. 5 shows a pattern of cured epoxy dots printed onto a silicon substrate, which was achieved within one single printing pass by using all 4 different levels of the greyscale printhead. The resulting dot diameters were between 85 μm for 15 pl drop volumes and 140 μm for the 60 pl drops. The height of the epoxy dots was found to be of the order of 4.5 μm for 15 pl drop volumes and 8 μm for 60 pl drop volumes. Smaller structure dimensions could be achieved when printing onto substrates with reduced wetting behavior, such as glass substrates. In this case the dot size was decreased to a range between 55 μm and 110 μm for the different volume levels between 15 pl and 60 pl.

With a large-drop printhead model, producing epoxy drop volumes of 180 pl, the resulting dot sizes were nearly 200 μm on silicon and 150 μm on glass substrates.

The process of using a printhead with a large number of printhead nozzles for the deposition of epoxy materials allows high deposition rates. With an XJ126-300 printhead that delivers epoxy drop volumes of 50 pl from each of its 126 channels at maximum drop repetition frequencies of 5 kHz, a continuous layer of around 8 μm thickness could be deposited at a rate of 42 cm^2 per second. Thicker layers can be achieved by applying a multi-pass printing approach and intermediate UV-curing steps. However, our investigations have shown that it is difficult to maintain a good structural control for thicker layers above 50 μm when printing with Epoxy X2.

A common problem for the dispensing process of fluidic media is the occurrence of overfill at areas of crossing line patterns, which results in an undesired flow-out of the liquid into the edge area (see Fig. 6a). Suitable compensation pattern could correct this and produce sharp edges at the crossing lines, as shown in Fig. 6b. This compensation was accomplished by reducing the number of deposited epoxy droplets at the area of the crossing lines. Further compensation to produce an undercut at the corners of the crossing lines was possible, as shown in Fig. 6c.

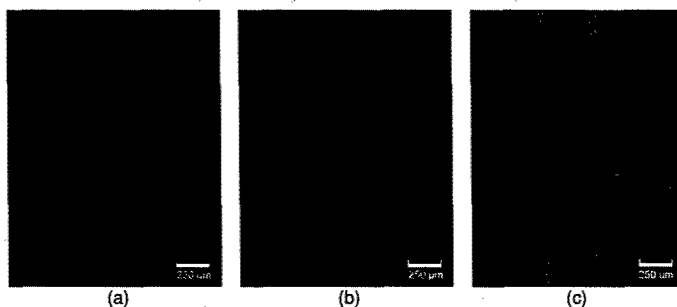


Figure 6. Optical micrographs of epoxy pattern at a crossing line pattern on a silicon substrate, (a) without compensation, (b) compensated for sharp edges, and (c) compensated for an undercut at the corners.

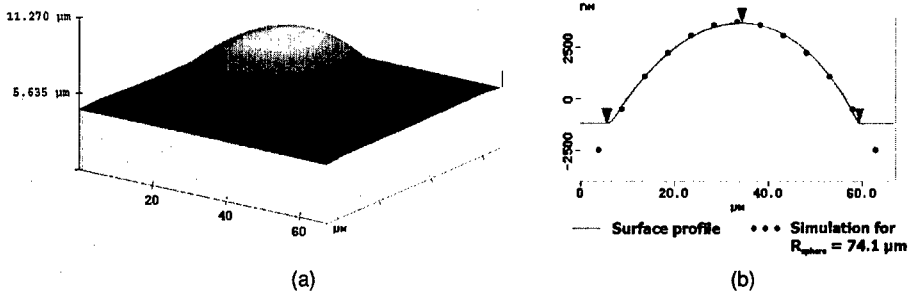


Figure 7. AFM image of a microlens deposited by direct inkjet printing, (a) topography image, (b) surface profile observed from the AFM measurement, together with a spherical fit.

Applications of this direct-write process for UV-curable epoxy materials would be in the fabrication and assembly of micro-fluidic biochips and MEMS devices. We have also applied this inkjet method for the production of micro-optical devices, specifically for the deposition of microlenses. Fig. 7a shows a topographic Atomic Force Microscope (AFM) image of such a microlens deposited onto a glass substrate, printed with a 15 pl droplet from the greyscale printhead. The AFM measurement yielded a diameter of 53 μm and a height of 5 μm for this lens.

Fig. 7b shows that the surface of the dot could be well fitted by a sphere with radius $R_s = 74.1 \mu\text{m}$, so that the dots represent planar convex lenses. With the focal length of a thin planar convex lens given by $f = R_s/(n-1)$, and the refractive index of $n = 1.522$ for Epoxy X2, a value of $f = 142 \mu\text{m}$ can be calculated for the deposited microlenses. A focal length in this range is for example particularly suited for optical fibre to device coupling applications.

In another experiment the deposition of composites consisting of magnetic materials in a polymeric matrix was investigated. These composites are intended for low- and medium density storage applications on disposable substrates, and for magnetic character recognition. In Fig. 8a such an inkjet printed magnetic pattern is shown.

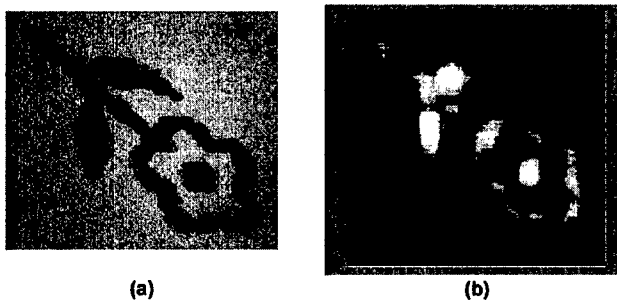


Figure 8. (a) Optical image and (b) map of the local AC-susceptibility of a magnetic test pattern inkjet printed with magnetic ink; brighter colors in the magnetic scan visualize larger magnitudes of the susceptibility (scan area was $3.25 \times 3.25 \text{ mm}$).

The magnetic material consisted in this case of nanosized $\gamma\text{-Fe}_2\text{O}_3$ particles. The magnetic nanoparticles were surface coated with polystyrene and dispersed in an organic carrier liquid. After drying of the printed structures the pattern was detectable by magnetic imaging. This detection was performed utilizing a novel 'in-plane' magnetic susceptibility imaging method developed recently [8]. Fig. 8b shows a mapping of the local distribution of the 'in-plane' susceptibility, measured for the inkjet printed pattern shown in Fig. 8a.

Further experiments to disperse magnetic nanoparticles in the UV-curable epoxy materials are currently in progress.

CONCLUSIONS

We have demonstrated in this work that a direct-write process of UV-curable epoxy materials could be achieved with high accuracy and high deposition rates using a multi-nozzle inkjet printhead. With this technique it was possible to produce dot array patterns and complex structure shapes in one printing sweep, addressing all 126 channels of the printhead individually. The epoxy dots can be deposited with a standard deviation of $2.3\text{ }\mu\text{m}$ and $2.6\text{ }\mu\text{m}$ in x- and y-direction. The control of the structure sizes of the deposited epoxy pattern was possible by variation of the droplet volumes.

The inkjet deposition technique could be used for the production of optical microlenses of almost perfect planar-convex shape. With a focal length of $142\text{ }\mu\text{m}$ these lenses appear suitable for micro-optical devices. Another promising application area of the direct-write process with inkjet printheads is the deposition of magnetic materials in a polymeric matrix for the production of magnetic information carriers.

ACKNOWLEDGEMENTS

This work was funded by the Swedish Agency for Innovation Systems (VINNOVA). The authors would like to thank Magnus Alsered from MA Kapslingsteknik, Sweden, for the consulting and characterization on epoxy materials, and Prof. S. Margel, Bar-Ilan University (RA), Israel, for the preparation of the magnetic nanoparticles.

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